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(54) MANUFACTURE OF POROUS SEPARATOR FOR BATTERY AND BATTERY USING THE SEPARATOR

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a porous separator member which is thin, easily manufactured, and manufactured at low cost by arranging separator precursor solution containing a solid granular material and polymer binder at a prescribed ratio on an electrode and changing this separator precursor solution into a porous composite separator to be jointed with the electrode.
SOLUTION: A thin layer of separator precursor solution is printed on an electrode surface of an electrochemical battery electrode. Second, the thin layer of the separator precursor solution is vulcanized on the electrode, so as to be changed into a microporous composite separator member. The separator precursor solution is constituted of an ink composed of a solid granular material, dispersed in polymer binder solution dissolved in appropriate solvent. It is preferable to use silica aerosol, which is a main component of a print separator for the solid granular material. In the separator precursor solution, the ratio of the binder to the solid granular material is selected between 5/95 and 50/50.

CLAIMS

[Claim(s)]

[Claim 1]It is a manufacturing method of a porous complex separator for electrochemical cells which has an electrode, A process of arranging a separator precursor solution included by a ratio which chose a ratio of this binding material [as opposed to this solid granular material for a solid granular material and a polymer binder] from the range of 5/95 to 50/50 on this electrode, A manufacturing method of a porous complex separator consisting of a process which changes this separator precursor solution to this porous complex separator joined to this electrode.

[Claim 2]The above-mentioned solid granular material Silica aerogel, gasification silica, silica gel, silica hydro-gel, silica xerogel, and silica -- sol and nature silica of colloid. Alumina, a titania, magnesia, kaolin, talc, diatomaceous earth, calcium silicate, a calcium carbonite, a magnesium carbonite, and a method according to claim 1 of being one sort chosen from a group of these mixtures.

[Claim 3]The above-mentioned polymer binders are polyvinyl chloride and polyvinylidene. Fluoride HEKUSA fluoropropylene A method according to claim 1 of being one sort chosen from a group of a copolymer and an ethylene propylene HEKUSADI ene monomer.

[Claim 4]A way according to claim 1 a process of arranging a separator precursor solution on the above-mentioned electrode is a process using printing technique.

[Claim 5]A method according to claim 1 of being the process of a process to which the above-mentioned separator precursor solution is changed on the above-mentioned electrode vulcanizing the above-mentioned separator precursor solution, and forming a porous separator layer.

[Claim 6]A way according to claim 5 the above-mentioned porous complex separator layer thickness is 5micro thru/or 100micro.

[Claim 7]A way according to claim 5 the above-mentioned vulcanization step includes a process of heating the above-mentioned separator precursor solution with a vacuum furnace in a temperature requirement of 90 to 130 **.

[Claim 8]A process of arranging a separator precursor solution which is a manufacturing method of a porous complex separator for electrochemical cells which has an electrode, and contains 60 to 95% of 1, 2, 3, and 4-tetrahydro naphthalene (THN) solvent both in quality and in quantity on this

electrode, A manufacturing method of a porous complex separator vulcanizing this separator precursor solution and consisting of a process of forming a porous complex separator stuck to this electrode.

[Claim 9]A way according to claim 8 a process of arranging a separator precursor solution on the above-mentioned electrode is a process using printing technique.

[Claim 10]A way according to claim 8 the above-mentioned vulcanization step includes a process of heating the above-mentioned separator precursor solution with a vacuum furnace in a temperature requirement of 90 to 130 **.

[Claim 11]Stick to the first electrode material layer and an electrode material layer of this first, constitute two or more micropores, and A solid granular material, A porous complex separator material layer provided on an electrode material layer of this first containing a composite construction which has a ratio [as opposed to this solid granular material of this binding material for a binding material holding this solid granular material] by a selected ratio between 5/95 and 50/50, being held in the second electrode material layer provided on the above-mentioned porous composite layer, and micropore of this plurality of the above-mentioned porous complex separator material -- this -- the first electrode material layer -- this -- an electrochemical cell having a liquid electrolyte which constitutes an electrical conduction medium between the second electrode material layer.

[Claim 12]The electrochemical cell according to claim 11 with which the second electrode layer includes material chosen from a group of an oxide, a sulfide, carbon compounds, metal, an alloy, intermetallic compounds, and these mixtures for a start [above-mentioned].

[Claim 13]The electrochemical cell according to claim 11 with which the above-mentioned liquid electrolyte contains ethylene carbonate, JIMECHIRU carbonate, and $LiClO_4$.

[Claim 14]The above-mentioned solid granular material Silica aerogel, gasification silica, silica gel, silica hydro-gel, silica xerogel, and silica -- sol and nature silica of colloid. Alumina, a titania, magnesia, kaolin, talc, diatomaceous earth, calcium silicate, a calcium carbonite, a magnesium carbonite, and the electrochemical cell according to claim 11 that is one sort chosen from a group of these mixtures.

[Claim 15]The above-mentioned binding materials are polyvinyl chloride and polyvinylidene. Fluoride HEKUSA fluoropropylene A copolymer and ethylene propylene HEKUSADIEN The electrochemical cell according to claim 11 which is one sort chosen from a group of a monomer.

[Claim 16]An electrochemical cell comprising:

The first electrode material layer.

It sticks to an electrode material layer of this first, two or more micropores are constituted, and it is a solid granular material.

A polymer binder.

With mass for melting this polymer binder, 60 to 95% of 1, 2, 3, and 4-tetrahydro naphthalene (THN) solvent, A porous complex separator material layer provided on an electrode material layer of this first containing a composite construction which has a ratio to this solid granular material of this binding material by a ratio selected between 5/95 and 50/50, Fluid ******** which is held in

micropore of this plurality of the second electrode material layer provided on the above-mentioned porous complex separator material layer, and the above-mentioned porous complex separator material layer, and constitutes an electrical conduction medium between an electrode material layer of the above first, and an electrode material layer of the above second.

[Claim 17]The above-mentioned solid granular material Silica aerogel, gasification silica, silica gel, silica hydro-gel, silica xerogel, and silica -- sol and nature silica of colloid. Alumina, a titania, magnesia, kaolin, talc, diatomaceous earth, calcium silicate, a calcium carbonite, a magnesium carbonite, and the electrochemical cell according to claim 16 that is one sort chosen from a group of these mixtures.

[Claim 18]The above-mentioned polymer binders are polyvinyl chloride and polyvinylidene fluoride HEKUSA fluoropropylene. A copolymer and ethylene propylene HEKUSADIEN The electrochemical cell according to claim 16 which is one sort chosen from a group of a monomer.

[Claim 19]An electrochemical cell which has a liquid electrolyte osmosis type separator, comprising:

An electrode.

A binding material which fixes this solid granular material that has chosen a ratio to the above-mentioned solid granular material from 5/95 to 50/50 so that a solid granular material layer and the; above-mentioned liquid electrolyte which were provided on this electrode that functions also as mechanical support may permeate into the above-mentioned solid granular material layer.

[Claim 20]The above-mentioned solid granular material Silica aerogel, gasification silica, silica gel, silica hydro-gel, silica xerogel, and silica -- sol and nature silica of colloid. Alumina, a titania, magnesia, kaolin, talc, diatomaceous earth, calcium silicate, a calcium carbonite, a magnesium carbonite, and the electrochemical cell according to claim 19 that is one sort chosen from a group of these mixtures.

[Claim 21]The above-mentioned binding materials are a polyvinyl chloride and polyvinylidene. A fluoride HEKUSAFURUORO propylene-copolymer and ethylene propylene HEKUSADIEN The electrochemical cell according to claim 16 which is one sort chosen from a group of a monomer.

[Claim 22]It consists of a solvent for melting a solid granular material, this binding material for solid granular materials, and this binding material, And a process of arranging on an electrode a solution which contained a ratio of this binding material to this solid granular material by a ratio chosen from between 5/95 to 50/50, and printing continuous layers of the above-mentioned separator, A manufacturing method of a microporous separator for electrochemical cells which has an electrode vulcanizing continuous layers of the above-mentioned separator and having the process of forming micropore there.

[Claim 23]The above-mentioned binding materials are a polyvinyl chloride and polyvinylidene. Fluoride HEKUSA fluoropropylene A copolymer and ethylene propylene HEKUSADIEN The manufacturing method according to claim 22 which is one sort chosen from a group of a monomer.

[Claim 24]The above-mentioned solid granular material Silica aerogel, gasification silica, silica gel, silica hydro-gel, silica xerogel, and silica -- sol and nature silica of colloid. The manufacturing method according to claim 22 made with alumina, a titania, magnesia, kaolin, talc, diatomaceous earth, calcium silicate, a calcium carbonite, a magnesium carbonite, and material chosen from a group of these mixtures.
[Claim 25]The manufacturing method according to claim 22 with which the above-mentioned vulcanization step includes a process of heating continuous layers of the above-mentioned separator on the above-mentioned electrode at about 90 to 130 ** all over a vacuum furnace.
[Claim 26]The manufacturing method according to claim 22 with which a process of printing continuous layers of the above-mentioned separator on an electrode uses either a stencil or screen-stencil art.
[Claim 27]An electrode and a matrix of a solid granular material which is dramatically thin so that it does not become independent, and is directly supported on this electrode, An electrochemical cell which has a liquid electrolyte osmosis type separator, wherein it holds this solid granular material to open matrix form which a liquid electrolyte can permeate and a ratio to this solid granular material has adhesives chosen between 5/95 and 50/50.
[Claim 28]The above-mentioned solid granular material Silica aerogel, gasification silica, silica gel, silica hydro-gel, silica xerogel, and silica -- sol and nature silica of colloid. The electrochemical cell according to claim 27 made with alumina, a titania, magnesia, kaolin, talc, diatomaceous earth, calcium silicate, a calcium carbonite, a magnesium carbonite, and material chosen from a group of these mixtures.
[Claim 29]About the above-mentioned binding material, they are a polyvinyl chloride and polyvinylidene. Fluoride HEKUSA fluoropropylene The electrochemical cell according to claim 27 made with material chosen from a group of a copolymer and an ethylene propylene HEKUSADI ene monomer.
[Claim 30]A manufacturing method of a microporous separator for electrochemical cells which has an electrode characterized by comprising the following.
It has 60 to 95% of 1, 2, 3, and 4-tetrahydro naphthalene (THN) solvent with mass for melting a solid granular material, this polymer binder for solid granular materials, and this polymer binder, A process of arranging on an electrode a solution which contains a ratio of this binding material to this solid granular material by a ratio chosen from between 5/95 to 50/50, and printing continuous layers of a separator.
A process of vulcanizing continuous layers of the above-mentioned separator and forming micropore there.

[Claim 31]The above-mentioned solid granular material Silica aerogel, gasification silica, silica gel, silica hydro-gel, silica xerogel, and silica -- sol and nature silica of colloid. The manufacturing method according to claim 30 made with alumina, a titania, magnesia, kaolin, talc, diatomaceous earth, calcium silicate, a calcium carbonite, a magnesium carbonite, and material chosen from a group of these mixtures.

[Claim 32]About the above-mentioned polymer binder, they are a polyvinyl chloride and polyvinylidene fluoride HEKUSA fluoropropylene. A copolymer and ethylene propylene HEKUSADIEN The manufacturing method according to claim 30 made with material chosen from a group of a monomer.
[Claim 33]The manufacturing method according to claim 30 which is a process for which a process of arranging the above-mentioned solution on the above-mentioned electrode uses printing technique.
[Claim 34]The manufacturing method according to claim 30 with which the above-mentioned vulcanization step includes a process of heating continuous layers of the above-mentioned separator on the above-mentioned electrode with a vacuum furnace in a temperature requirement of 90 to 130 **.
[Claim 35]An electrode.
It is an opening among particles directly supported on this electrode.
Are the electrochemical cell provided with the above and this silica particle layer has a binding material which holds this silica particle for a silica particle, A discontinuous and vulnerable silica particle layer which has chosen a rate over this silica particle of this binding material from 5/95 to 50/50 and which has an opening among particles directly supported on this electrode, and a fluid organic solution electrolyte held in the above-mentioned opening are included.

[Claim 36]About the above-mentioned binding material, they are a polyvinyl chloride and polyvinylidene. Fluoride HEKUSA fluoropropylene A copolymer and ethylene Propylene HEKUSADIEN The electrochemical cell according to claim 35 made with material chosen from a group of a monomer.
[Claim 37]The electrochemical cell according to claim 35 which formed the above-mentioned fluid organic solution electrolyte including 1.0M $LiClO_4$ to a solvent mixture which consists of ethylene carbonate 2 volume part and JIMECHIRU carbonate 1 volume part.
[Claim 38]An electrochemical cell which is provided with the following and to which a ratio of specific resistance of this electrolyte to specific resistance of a separator filled up with this electrolyte is characterized by being larger than 0.10 by a result of compound impedance measurement with sine voltage of 5V in a frequency domain (100 or 000 Hz thru/or 0.01 Hz).
An electrode.
A discontinuous and vulnerable layer of a silica particle which has an opening among particles which has a binding material holding a silica particle, had chosen a rate over the above-mentioned silica particle of this binding material from 5/95 between 50/50, adjoined this electrode and was provided.
A fluid organic solution electrolyte contained in the above-mentioned opening.

[Claim 39]The electrochemical cell according to claim 38 which contains 1.0M $LiClO_4$ in a solvent mixture in which the above-mentioned fluid organic solution electrolyte consists of ethylene

carbonate 2 volume part and JIMECHIRU carbonate 1 volume part.

[Claim 40]About the above-mentioned polymer binder, they are polyvinyl chloride and polyvinylidene. Fluoride HEKUSA fluoropropylene A copolymer and ethylene propylene HEKUSADIEN The electrochemical cell according to claim 38 made with material chosen from a group of a monomer.

[Claim 41]The above-mentioned solid granular material Silica aerogel, gasification silica, silica gel, silica hydro-gel, silica xerogel, and silica -- sol and nature silica of colloid. The electrochemical cell according to claim 38 made with alumina, a titania, magnesia, kaolin, talc, diatomaceous earth, calcium silicate, a calcium carbonite, a magnesium carbonite, and material chosen from a group of these mixtures.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]Especially this invention relates to the art which forms an electric insulation separator between the two conductive surfaces about an electrochemical cell and its manufacture.
[0002]
[Description of the Prior Art]In micro electronic technology, the tendency of large-scale integration continues and research of a new material for small and quality electronic equipment or a new manufacturing method is advanced also in the electronics industry. portable electronic machines especially, such as a portable computer, a telephone, an audio, video equipment, and a pacemaker, -- research on manufacture of dexterous high energy and the Electrochemistry Sub-Division power supply of high power density is advanced.
[0003]Increase of the output per unit capacity and the improvement in a discharge characteristic have started whether a thinner separator layer is provided and the electrochemical cell of a reliance thin shape can be manufactured. Maintenance and reliability of a thin separator (less than 50micro) are dramatically important, and concern is increasing in these for these ten years. A separator separates a negative electrode (anode) from an anode (cathode) physically and electrically within an electrochemical cell, and has a function which prevents a short circuit within a cell. The separator must be an electric insulation material. The separator must make possible further ion migration between a negative electrode and an anode. Usually, a separator comprises two or more mats, a pellet, paper, and a polymer sheet, and contains the electrolyte in those circulating hole structures.
[0004]A separator sticks with a negative electrode and an anode, and ionic conduction arises by charge or discharge of an electrode through the electrolyte phase in the stoma which a separator follows. So, it must be dimensionally stable, and it is porosity, electrolyte absorptive power and holding power of a separator must be high, and its ionicity-proof must be low. A separator needs pliability again. The separator must be able to correspond to the electrochemical expansion and contraction which are produced in a negative electrode and an anode during discharge and/or

charge. It must be able to correspond also to thermal expansion of a cell and contraction.
[0005]Oxidation resistance and reduction resistance are also required for a separator. It must be insolubility in an electrolyte. It must have corrosion resistance to the resultant produced within other components of a cell, or a cell. The physicochemical characteristic of a separator must harmonize with the device and method which are used for manufacture of an electrochemical cell. A separator must be thermally stable at the time of use at the time of storage at the time of manufacture of an electrochemical cell.
[0006]Finally, in order to make ionicity-proof into the minimum, a separator must be made as thin as practically possible in consideration of the manufacturing method and the performance to wish of an electrochemical cell. a conventional example -- gasification silica, silica gel, Celica aerogel, silica xerogel, silica hydro-gel, and silica -- a part of these characteristics were able to be obtained by using silicon oxide materials, such as sol and nature silica of colloid. The material the outside of it called alumina, magnesia, kaolin, talc, diatomaceous earth, calcium silicate, ARUMINUMU silicate, calcium carbonate, and magnesium carbonate is also used as the inactive filler of a separator, an extender, and a circulating hole formed material.
[0007]In the conventional example, various separator / electrolyte structures for electrochemical cells are developed by applying various such materials. Generally, structure is constituted conventionally [these] as ion electric conduction gel, a pellet, an ion electric conduction solid, and a liquid electrolyte restoration porous separator. For example, in one conventional example, gasification silica is used as a gelling agent of a chloride electrolyte. Silica salt acid gel is impregnated with polymerization foam, and constitutes the ion sorting separator member for oxidation reduction cells to be moved by chloride ion. Similarly, in other conventional examples, silica gel is used for immobilization of a sulfuric acid electrolyte, and the manufacturing method of a sealing dry type storage battery is provided.
[0008]For example, in thermojunction art, a separator member is manufactured by a different method. Electrolyte salt is mixed with gasification silica, and a separator member presses melt in a pellet type, and is manufactured. The obtained pellet type separator is allocated between the anode and negative electrode of a thermojunction cell. With heating, the electrolyte salt in a pellet is fused, shows ion conductivity, and activates a battery cell. In an elevated temperature, a thermojunction separator member is held by the capillary force of the fused salt in a porous gasification silica matrix, and does not need other binding materials for separator shape maintenance.
[0009]However, this art is not applied to manufacture of the ordinary temperature type battery cell. This has the weak capillary force of most electrolytes of an ordinary temperature type cell, and is because it is insufficient for maintenance of the silica electrolyte structure where it does not restrain. So, it is heavy-gage in the separator for ordinary temperature type cells, and size and shape are restricted. In thin film battery art, chloridation gasification silica or alumina is used as an inorganic bulking agent for solid electrolyte creation. This electrolyte membrane is constituted combining a polymer matrix material, electrolyte salt, a compatibility solvent (plasticizer), a cross linking agent, and a detailed packing material. Structure is non-porosity and is a polymer

electrolyte film of being flexible and a become [independent] type.

[0010]In this electrolyte membrane, ionic conduction arises according to a solid state in electrolyte plasticization polymer. In particular, by addition of an inorganic bulking agent, the physical intensity of an electrolyte membrane improves and the substitution of an electrolyte absorption level and a plasticizer increases substantially. As a result, the purpose that become unnecessary [a separator] and a solid electrolyte separates the negative pole from the anode is achieved. In thin film battery art, a solid-electrolyte membrane can print easily on the surface of an electrode member using screen printing or a stencil-printing method. However, if the separator member of a different body is not provided, an electrolyte will be compressed and the short circuit and/or displacement of an electrode member will be caused. In practice, this state is improved by screen-stencil, the "stud" by which stencil printing was carried out, or a "standoff", and an electrode member and a solid electrolyte member are strengthened to compression.

[0011]However, when the ion conductivity of a solid electrolyte is low and especially charge and/or discharge of high rate are required, use of a thin film battery is restricted. Stencil printing of a "stud" or the "standoff" is screen-stenciled or carried out like the surface of the electrode member of an electrochemical capacitor, and it is obtained. In this case, in order to raise the intensity of a standoff, silica reinforcement epoxy polymer is used.

[0012]The efforts greater than before to manufacture of the silica content microporous separator structure using a liquid electrolyte are made. There is a complex separator which contains the microporous silica separator, silica filler, and polymer binder which consist of organic silicon polymer as an example of this structure. In rechargeable battery art, it can form, for example by making an organic silicon polymer solution disassemble on the 3 yuan transition metal oxide electrode which lithiated the ultra thin type layer of the microporous silica separator. At the time of manufacture, the film of an organic silicon polymer solution is applied on the surface of a cell electrode. After the desiccation for solvent removal, a coat is vulcanized, and turns into a vitrified film, and plasma oxidation is carried out after that, and it forms micropore in a film. The silicate film which has puncturing by the shape of acquired **** acts as a separator. However, it must take care so that an active electrode may not oxidize by plasma more than needed.

[0013]In the conventional example, the above-mentioned silica or many of non-silica fillers are used for manufacture of the microporous cell separator which has a composite construction. These fillers are used as a medium which strengthens the polymer binder used for manufacture of a separator while they are made as a particle separated minutely and make a microporous separator porosity. With the complex special feature of a separator material, a separator shows high intensity and high flexibility.

[0014]In a typical method, a binding material is mixed to a solid granular material, a still more suitable solvent is mixed, and a paste is formed. A porous separator is obtained while removing a solvent by extruding this paste, considering it as a sheet shaped, and vulcanizing this sheet material after that. In early stages, silica gel was used as the inorganic filler and extender for microporous separators containing a polymeric polyolefin binding material. Similarly, sedimentation amorphous silica was used for manufacture of a microporous polymer battery separator. The

polymeric material was strengthened with these separators using a small amount of (30% or less) silica, and it was considered as porosity with them.

[0015]In another conventional example, it consists of polymer and a silica filler, and there is also a battery separator with which a combined matrix contains a silica filler a maximum of 97%. In this case, as a filler, precipitated silica or gaseous silica is preferred. However, if a lot of [in this way] silica fillers are contained, it will have an adverse effect on the mechanical property of a separator, and the intensity and pliability will be reduced. In order to solve these problems, by extruding and laminating the above-mentioned complex separator member to both sides of a fibrous polymer sheet conventionally, the intensity and pliability of the separator member were raised and independence nature was given.

[0016]Although the functional complex separator was obtained by the above-mentioned conventional method, these methods provide a comparatively thick separator layer, cause excessive isolation to inter-electrode, and increase the total resistance of a separator. Since output is very small, there is a problem in the handling of the material under manufacture, and a manufacturing cost and a labor increase. Similarly, since there is no compatibility in adhesion with an electrode and a separator member, positioning exact [the separator member in the Electrochemistry Sub-Division battery structure] and positive is barred, and cell capacity is made useless. The interval between cells increases by such inefficient attachment of an electrochemical cell, and battery efficiency falls further.

[0017]A deer is carried out, silica and polymer are used for manufacture of the separator for Electrochemistry Sub-Division power supplies, and a printing method is used for manufacture of the detailed upheaval separator for the solid electrolyte for printing Electrochemistry Sub-Division power supplies, and charge storage devices.

[0018]

[Problem(s) to be Solved by the Invention]However, a conventional example is not provided with a means to attain all the characteristics of the most suitable separator while it manufactures the printing porous separator for liquid electrolyte power supplies. a thin shape -- manufacture -- it is easy, and is cheap and the separator member which is [at chemical inertness] thermally stable in electrochemical inertness and insolubility, and is joined with sufficient compatibility by lyophilicity with porosity is preferred.

[0019]An object of this invention is to provide a chemical cell with the manufacturing method of this separator, and this separator.

[0020]

[Means for Solving the Problem]The above-mentioned purpose is attained by a method of this invention of having a process of printing a film of a separator precursor solution to an electrode surface of the Electrochemistry Sub-Division cell electrode, and a process which vulcanizes a film of a separator precursor solution on an electrode, and is changed to a microporous complex separator member. A separator precursor solution comprises ink which consists of a solid granular material distributed in a solution of a polymer binder melted into a suitable solvent. In a preferred embodiment, a solid granular material is silica aerogel and forms main structure material of a

printing separator. In a separator precursor solution, a ratio to a solid granular material of a binding material is chosen between 5/95 thru/or 50/50.

[0021]As for a polymer binder of an ink solution, it is preferred that an ethylene propylene HEKUSADI ene monomer (EPDM) is included. An ink solution contains a 1,2,3,4-tetrahydro naphthalene (THN) solvent for melting an ethylene propylene HEKUSADI ene monomer (EPDM) again. Content of a solvent in an ink solution is 60 to 95% of range both in quality and in quantity.

[0022]Carrying out a deer, a separator object on an electrode plate comprises network structure of circulating hole space and a solid separator object containing a particle mutually joined with a polymer binder. As a result, a separator serves as a porous composite layer on an electrode of an electrochemical cell. This structure is un-becoming [independent] nature, it is ultra-thin, and is supple, and is joined with sufficient compatibility to an electrode surface under it. There are many modes in this invention. In one mode of this invention, a manufacturing method of a porous complex separator for electrochemical cells which has an electrode is provided. This method consists of a process of arranging a separator precursor solution on an electrode, and a process of forming a porous complex separator which a separator precursor solution is changed and is stuck to an electrode. A separator precursor solution contains a particle and a polymer binder. A ratio to a granular material of a polymer binder is chosen between 5/95 and 50/50.

[0023]In another mode of this invention, a manufacturing method of a porous complex separator for electrochemical cells which has an electrode is provided. This method consists of a process of arranging a separator precursor solution on an electrode, and a process of forming a porous complex separator which vulcanizes a separator precursor solution and is stuck to an electrode. A separator precursor solution contains 60 to 95% of 1,2,3,4-tetrahydro naphthalene (THN) solvent both in quality and in quantity.

[0024]In another mode of this invention, an electrochemical cell which has the first electrode material layer is provided. An electrochemical cell consists of a porous complex separator material layer provided on the first electrode material, the second electrode material layer provided on a porous composite layer, and a liquid electrolyte. A separator material is stuck to the first electrode material layer, and constitutes two or more micropores. A liquid electrolyte is contained in a circulating hole of plurality of a porous complex separator material, and an electrolyte serves as an electrical conduction medium between the first and second electrode layers.

[0025]A separator material has a composite construction which consists of a binding material holding a solid granular material and a solid granular material. A ratio to a solid granular material of a binding material is chosen between 5/95 and 50/50. In another mode of this invention, an electrochemical cell which has the first electrode material layer is provided. An electrochemical cell consists of a porous complex separator material layer provided on the first electrode material, the second electrode material layer provided on a porous composite layer, and a liquid electrolyte. A separator material is stuck to the first electrode material layer, and constitutes two or more micropores. A liquid electrolyte is contained in a circulating hole of plurality of a porous complex separator material, and an electrolyte serves as an electrical conduction medium between the first and second electrode layers.

[0026]A separator material has a composite construction made from mass for melting a solid granular material, a polymer binder, and a polymer binder with 60% thru/or 95% of 1,2,3,4-tetrahydro naphthalene (THN) solvent.A ratio to a solid granular material of a binding material is chosen between 5/95 and 50/50. An electrochemical cell which has a liquid electrolyte-pervious separator is provided in mode of this invention another again. An electrochemical cell contains a solid granular material layer directly supported on an electrode for mechanical support, and a binding material for solid granular materials. A ratio to a solid granular material of a binding material is chosen between 5/95 and 50/50 so that the above-mentioned liquid electrolyte may permeate through a solid granular material layer.

[0027]In another mode of this invention, a manufacturing method of a microporous separator for electrochemical cells which has an electrode is provided. A method arranges a solution containing a solid granular material, a binding material for solid granular materials, and a solvent for melting a binding material, on an electrode, it prints continuous layers of a separator, vulcanizes this layer after that, and forms micropore. A ratio to a solid granular material of a binding material is chosen between 5/95 and 50/50.

[0028]In another mode of this invention, an electrochemical cell which has a liquid electrolyte-pervious separator possessing an electrode is provided. A separator is provided with the following. A solid granular material matrix directly supported on an electrode in order are thin and not to become independent.

Enough binding materials to hold a solid granular material to open matrix form voice which a liquid electrolyte permeates in a solid granular material layer.

A ratio to a solid granular material of a binding material is chosen between 5/95 and 50/50.

[0029]In another mode of this invention, a manufacturing method of a microporous separator for electrochemical cells which has an electrode is provided. A method arranges a solution which consists of 60% thru/or 95% of 1,2,3,4-tetrahydro naphthalene (THN) solvent with mass for melting a solid granular material, and a polymer binder for solid granular materials and a polymer binder, A process of joining continuous layers of a separator with sufficient compatibility on an electrode, and a process of vulcanizing this layer after that and forming micropore are included. A ratio to a solid granular material of a polymer binder is chosen between 5/95 and 50/50.

[0030]An electrochemical cell which has an electrode is provided in another mode of this invention. An electrochemical cell has a layer which is a silica particle and which continues although it is weak. A silica particle is discontinuous and an opening is in between. There is no gap in this layer, and since it is continuing, a short circuit does not arise in inter-electrode [which approaches mutually]. A layer is weak, namely, since there is no independence nature, it is directly supported by electrode and a fluid organic solution electrolyte is contained in an opening. A discontinuous layer contains a binding material for holding a silica particle, and a ratio to a silica particle of a binding material is chosen between 5/95 and 50/50.

[0031]An electrochemical cell which has an electrode is provided in another mode of this invention. An electrochemical cell adjoins an electrode, and has a discontinuous weak layer which consists of a particle which has an opening in between, and a fluid organic solution electrolyte is contained in

an opening. This weak layer contains a binding material for holding a particle, and a ratio to a particle of a binding material is chosen between 5/95 and 50/50. A ratio to specific resistance of a separator filled up with an electrolyte of electrolytic specific resistance is larger than 0.10 in 100 or 000 Hz of frequency domains thru/or 0.01 Hz, and compound impedance measurement in sine voltage of 5 mV.

[0032]

[Embodiment of the Invention]The other purpose and advantage will become clearer enough than the next explanation indicated in relation to the accompanying drawing along [said] this invention. As shown below, the method of a preferred embodiment prints an ink-like separator precursor selectively on an electrode plate, and provides the manufacturing method of the microporous junction silica separator which carries out after cure and is made into the microporous structure where the electrolyte of an electrochemical cell can be held.

[0033]As for an example of the method of forming a microporous separator from an ink solution, these people are indicated to manufacturing method" of the porous separator for U.S. application number 08/767,468" Electrochemistry Sub-Division power supplies under present application. The contents of this application are mentioned here. In this method, an ink solution is obtained by distributing silica aerogel in the BEEA solvent (2 (2-butoxyethoxy) ethyl acetate) containing a PVDF binding material (polyvinylidene fluoride HEKUSAFURORO propylene copolymer). In this method, a BEEA solvent is evaporated first and the two-step heat treatment method of vulcanizing a separator continuously is used.

[0034]As improvement of this method, by the method of this invention, after a separator ink solution melts an EPDM binding material (ethylene-propylene-HEKUSADIEN monomer) in THN (1,2,3,4-tetrahydro naphthalene), it is obtained by adding this solution to silica aerogel. In this new method, it ends by one heat treatment.

[0035]Next, it explains according to figures. The number same in the inside of a figure shows the same portion. Drawing 1 shows the Electrochemistry Sub-Division battery structure 10 which consists of three laminations, the negative electrode layer 29, the separator/electrolyte layer 24, and the positive electrode layer 19. Each electrode layer has the active materials 15 and 16 (electrode) formed on the electrode substrates 20 and 30 and the substrate 20 and 30. The substrates 20 and 30 constitute the electrode 15 and the charge collector for 16, and send current in charge and the discharge cycle of the electrochemical cell 10. A separator layer has the separator member 25 which was stuck with the negative electrode active material 15 and the positive active material 16, and was provided.

[0036]According to this invention, the separator member 25 of the electrochemical cell 10 consists of a porous composite material. It has the performance superior to the conventional separator possessing a granular reinforcing member while it has high performance and can make a cell small unprecedentedly, even if the separator layer 25 obtained by this invention is dramatically thin. A porous combined-matrix structure of the separator member 25 of this invention is shown to drawing 2 by the microscope level, and consists of a suitable mixture of the particle 32 and the polymer binder 34 which are made by vulcanizing a separator precursor solution. A separator precursor

constitutes the ink which consists of a solid granular material distributed in the polymer binder solution which melted into the solvent. This Separator, Inc. is printed by the surface of the electrode active materials 15 and 16 (a negative electrode and/or anode), and a solvent is removed by evaporation and forms a separator member.

[0037]The separator 25 of this invention is thin and the structure which is supple with porosity is produced by ink composition which prints presswork and the separator 25. To the electrolyte of the electrochemical cell 10, as for the solid granular material which is a main material of the printing separator 25, it is desirable that it is lyophilicity, and it needs to be distributed in the solvent of printing ink. Although the material in particular used as a solid granular material is not limited, silica aerogel, Gasification silica, silica gel, silica hydro-gel, silica xerogel, silica -- sol, the nature silica of colloid, alumina, a titania, magnesia, kaolin, talc, diatomaceous earth, calcium silicate, aluminium silicate, calcium carbonate, magnesium carbonate, and such combination exist.

[0038]When using the separator of this invention for the electrochemical cell containing an alkaline electrolyte solution, alumina and magnesia are accepted to be a suitable granular material. On the other hand, when using the separator of this invention for the electrochemical cell containing an acid electrolyte solution or an electrolyte nonaqueous solution, silica gas, silica gel, silica hydro-gel, silica xerogel, and silica aerogel are accepted to be a suitable granular material.

[0039]The suitable granular material considered now is the silica aerogel by which humidity may be carried out with most Electrochemistry Sub-Division battery electrolytes. Silica aerogel is promising especially as a material which may be distributed simply in a suitable ink solvent. About 0 and the range of suitable particle diameter are 01 to about 3.0 micro. Although various surface treatment does to aerogel for the improvement in dispersibility, aerogel is cheap, is a high grade and can be used with particle diameter suitable for suitable presswork.

[0040]It is known by the person skilled in the art that a polymer binder comprises a mixture of single polymer and polymer or a mixture of polymer and a copolymer. Although a monomer may be included in ink, separator printing postpolymerization is carried out. Polymer in ink may construct a bridge by chemical or suitable exposure after separator printing. To the binding material used for these purposes, polyvinyl chloride (PVC), Polyvinylidene Fluoride HEKUSAFURUORO propylene vinylidene A copolymer (PVDF) and ethylene-propylene-HEKUSADIEN Ethylene-propylene-HEKUSADIEN known also as an elastomer (EPHE) There is a monomer (EPDM).

[0041]In the method of a preferred embodiment, a separator ink solution melts binding material polymer in a solvent, and is formed by distributing a solid granular material in a binding material-solvent solution after that. Binding material polymer is mixed with a solid granular material, and in order to make the more uniform separator member 25, various instruments like a blender are used. a ratio [suitably as opposed to the solid granular material of a polymer binder in Separator, Inc.] -- the range of about 5/95 to 50/50 -- it is constituted so that it may become the range of 20/80 to 40/60 more preferably. As long as it is required, other materials may also be included in ink.

[0042]For example, the material which reforms the surface of a particle for the improvement in wettability may be used. such a material is publicly known -- magnesium silica fluoride or triton X-

100™ (Union Carbide.) A surface-active agent like Danbury, CT, SARUFINORU™ (exhaust air products, TSURENTON, NJ), or Fluorad ™ (3M, St. Paul, MN) is the example. Separator, Inc. of this invention may consist of mixtures of the solid which has compatibility with the material of an electrochemical cell, and an ink material.

[0043]The solvents which melt a polymer binder, or those mixtures may be sufficient as the solvent used by this invention. Especially a desirable solvent is THN (1,2,3,4-tetrahydro naphthalene) which may be obtained from an ARUDOURIHHI chemical company, Milwaukee, and Wisconsin. Usually, the solvent content of Separator, Inc. is 60 to 95% of range both in quality and in quantity. However, this range is determined by the kind and printing method of a binding material and silica. If the ratio to the particle of a polymer binder is decided, a presentation and rate of a solvent will be adjusted so that the viscosity of ink may be suitable for the following presswork.

[0044]In suitable working example, a separator ink solution is hypoviscosity comparatively at the time of stirring, and has hyperviscosity comparatively at the time of stillness. A deer is carried out, and it is mobility, and an ink solution has the feature which serves as non fluidity at the time of printing to an electrode surface while making presswork possible. So, in presswork, an ink solution can be easily applied to an electrode surface using a publicly known screen or stencil-printing art. However, once it applies to an electrode surface, an ink solution will be stopped and stuck to an application part.

[0045]After preparing Separator, Inc., this precursor is painted [publicly known] and printed with a printing method on the surface of an electrode active material (an anode and/, or negative electrode). In electronics or graphic arts, in order to print thick film ink and/or soldering paste, the screen and the stencil-printing method are used widely. Usually, ink is extruded from the screen in which the pattern was formed, or a stencil, using squeegee, and a printing pattern is formed. Therefore, the screen printer which may be obtained from DEHATO of the MPM corporation of Massachusetts and Franklin or Massachusetts, and Bull Linton is used. However, if it is a person skilled in the art, it will be clear that presswork's of a preferred embodiment it can carry out using known art, such as other printings and paint art.

[0046]In a preferred embodiment, Separator, Inc. is first printed by the electrode plate. Separator, Inc. is vulcanized from about 8 by a 1 to 200-torr pressure range in the temperature requirement of 90 to 130 ** in a vacuum furnace after that for 15 hours. In this temperature requirement, both removal of a solvent and vulcanization of a binding material are performed. Therefore, heat treatment can be performed at one process. The thickness of the separator member formed on an electrode is controlled by the viscosity and presswork of Separator, Inc.

[0047]It must recognize that the deformation condition from Separator, Inc. to a separator is decided with the polymer binder chosen. For example, when binding material polymer is polymer which can be UV vulcanized, a vulcanization step may also be performed using UV vulcanization art. When using the polymer binder (for example, urethane) which can be UV vulcanized, after-desiccation UV light vulcanizes a binding material at 90 to 130 **. When a binding material is polymer (for example, silicon resin) which can be vulcanized catalytically, a vulcanization step can

be catalytically performed at nominal temperature (for example, 150 **).

[0048]The separator object on an electrode plate is constituted from network structure of circulating hole space and the solid separator object which consists of a particle joined with the polymer binder by the vulcanization step, as shown in drawing 2. In practice, the solid part of a separator is arranged at an electrode plate, and constitutes the composite construction joined with sufficient compatibility to an electrode plate. The composite construction has the rigidity of a particle, and the pliability of a polymer binder. As a result, since the high mechanical strength of an electrode is used for mechanical support, it is thin, the complex separator member of un-becoming [independent] nature is formed, and it gets.

[0049]The thin film separator 25 (drawing 1) of this invention forms the laminated structure which was joined with sufficient compatibility to the electrode active material surface, and was united with porosity, solves a blank-layout treatment problem substantially, and makes possible a non-self-standing ultra thin type separator. The complex separator member of this invention may be arranged, positioned and joined to any suitable electrode structures whose geometry suits to a printing method by the presswork of this invention. If a separator is printed on the electrode by which the surface active materials 15 and 16 were printed with the similar printing method, it is still more advantageous on manufacture.

[0050]That is, it is advantageous especially if the same solvent and binding material as the solvent and polymer binder which are used for printing of the active materials 15 and 16 of an electrode are used for Separator, Inc. In this case, the generated lamination separator / electrode structure do not have change in binding material composition at a separator/electrode interface including the same binding material. This interface has carrying out [little] cleavage by the thermal and electrochemical expansion or contraction produced during manufacture and an operation. Both members are substantially strengthened by the arrangement and junction to the electrode member of a separator member, and attachment of an electrochemical cell becomes easy. A deer is carried out and the time-consuming work mutually needed conventionally for the separator of a different body, manufacture of an electrode member, positioning, and attachment by this process is removed.

[0051]According to a laminating process given in here, when the separator member of the same presentation must be treated separately, the separator of the thickness of five to 100 impossible micro becomes possible. Being able to carry out direct production of the ultra thin type separator which cannot be manufactured as a different body on the adjoining electrode, since it is vulnerable, an electrode gives intensity required for separator support.

[0052]The separator of this invention may be printed on the positive electrode member, the negative electrode members, or the two-electrodes surface of an electrochemical cell, as long as separator ink solvents are an electrode material and compatibility. These electrode members consist of an oxide, a sulfide, carbon compounds, metal, an alloy, and an intermetallic compound. A separator may be printed again to the carbon negative electrode charge collector of the cell using liquefied anode battery depolarizers, such as a carbon negative electrode of a lithium ion cell or chloridation thionyl, and sulfurous acid. An electrode active material consists of active materials,

such as a manganic acid ghost, a cobalt oxide, a vanadium oxide, or a nickel oxide, or those mixtures. An inert filler, an electric conduction additive agent, and a binding material may also be mixed with an electrode member. The separator of this invention may be printed on such a composite construction again.

[0053]After forming a porous separator member, it distributes in a separator, other electrodes are firmly forced on a separator after that, and an electrolyte forms an electrochemical cell. The electrochemical capacitor often called a super capacitor and an ultra capacitor with an electrochemical cell in this invention, The electrolysis cell used for the Electrochemistry Sub-Division composition and/or the Electrochemistry Sub-Division decomposition of an electrolytic condenser, primary and a rechargeable battery, a fuel cell, an electrochemical sensor, and a compound is included. In one mode of this invention, if filled with an electrolyte, the separator which becomes transparent optically is provided, and these separators are used also with the electrochemical cell using a photon auxiliary oxidation-reduction reaction.

[0054]Change which suits a different use and conditions is possible for this invention. Many examples shown below are the things for explanation of this invention, and this invention is not limited to these.

It was obtained by example 1 Separator, Inc. dissolving an EPDM binding material (an ethylene-propylene-HEKUSADIEN monomer, NORDEL^R hydrocarbon rubber 2722EPEL, E. I. du Pont de Nemours elastomer) in THN (1,2,3,4-tetrahydro naphthalene) 95% 5%. This solution was added to the silica aerogel (surface treatment of SilCRON^{R}G-130,300 m^2/g, an SCN corporation, and this aerogel is carried out, and distribution in an ink solvent is improved) of weighing. The solution was added to silica aerogel until the ratio of a binding material and silica became 40/60. This paste was mixed on 3 roll mills. During this work, solvent composition was adjusted so that ink viscosity might turn into viscosity suitable for subsequent printing. Usually, the solvent content of ink is 60% to 90%.

[0055]The above-mentioned ink was screen-stenciled by the pattern of the rectangular head on the aluminium foil charge collector. 110 ** of adhering ink was dried all over the vacuum furnace after that for 10 hours. The temperature and time of this heating process are decided by thickness of a solvent, the binding material used for ink manufacture, and adhering ink. The thickness of the separator was measured by a micrometer after this heating process. The separator was 17micro. An electrolyte (it is 1.0M $LiClO_4$ to the solvent mixture which consists of ethylene carbonate 2 volume part and JIMECHIRU carbonate 1 volume part) is distributed by the separator, and the counterelectrode of aluminum is pushed against a separator and forms aluminum / separator / aluminum cell.

[0056]the ratio of an electrolyte restoration separator -- ion resistance calculated from the compound impedance measurement value at the time of the reactance 0 of aluminum / separator / aluminum cell. The ion conduction efficiency of a separator is expressed with rho**/rho. Here, rho** is electrolytic specific resistance and rho is the measurement specific resistance of an electrolyte restoration separator. In this cell, it is rho**/rho=0.31.

example 2 Separator, Inc. -- silica aerogel (SilCRON^{R}G-130,300-m^2/g and an SCN corporation.) surface treatment of this aerogel is carried out, and distribution in an ink solvent is improved -- **** -- it was obtained by carrying out dry mixing with a PVDF binding material (a polyvinylidene fluoride HEKUSA fluoropropylene copolymer, KYNAR^{R}Flex 2801, Elf Atochem). This mixture was gradually added to the ink solvent (BEEA, 2 (2-butoxyethoxy) ethyl acetate), and formed the paste. The paste was mixed on 3 roll mills. The remainder of the aerogel PVDF mixture was mixed by paste state on 3 roll mills. Ink was adjusted so that it might become a ratio of 15 copies of PVDF binding materials to 85 copies of silica aerogels. The range of this ratio is about 5:95 (PVDF: silica aerogel) to 33:65. When printing a thin separator, higher PVDF content is preferred and low PVDF content is used for a thick separator. PVDF: After deciding the ratio of silica aerogel, solvent composition was adjusted so that ink viscosity might turn into viscosity suitable for the next screen-stencil. Usually, the solvent content of ink is 60% to 75% both in quality and in quantity.
[0057]The above-mentioned ink was screen-stenciled by the pattern of the rectangular head on the nickel charge collector. 100 ** dried all over the vacuum furnace after that for 16 hours (a BEEA solvent is removed), and 210 ** of adhering ink was dried in the convection furnace after that for 10 minutes (a PVDF binding material is dissolved). The temperature and time of these two heating processes are decided by thickness of a solvent, the binding material used for ink adjustment, and adhering ink. The thickness of the separator was measured by a micrometer after this heating process. The separator was 55micro.
[0058]An electrolyte (it is 1.0M $LiClO_4$ to propylene carbonate) is distributed in a separator, and the counterelectrode of nickel is pushed against a separator and forms nickel / separator / nickel cell. The compound impedance of this cell was measured using the sine voltage amplitude of 5 mV over a 100 or 000 to 0.01-Hz frequency range. the ratio of an electrolyte restoration separator -- ion resistance calculated from the compound impedance measurement value in case the reactance of nickel / separator / nickel cell is 0. In this cell, it is rho**/rho=0.39.
The same test as Example 2 was made except having replaced with example 3 silica aerogel and alumina having been used for Separator, Inc. by the ratio of 70 copies to 30 copies of PVDF(s). The thickness of this separator was 97micro. It is rho**/rho=0.39.
The same test as Example 2 was made except having replaced with example 4 silica aerogel and the titania having been used for Separator, Inc. by the ratio of 85 copies to 15 copies of PVDF(s). The thickness of this separator was 77micro. It is rho**/rho=0.10.
[0059]Although the deer was carried out, and the description about the preferred embodiment of this invention was shown and has described and pointed out the fundamental and new feature of this invention, if it is a person skilled in the art, unless it will separate from the pneuma of this invention, it is clear that various abbreviations and substitution are carried out and a change can be made to the device, a method, and a use. Therefore, the range of this invention is not restricted to the above-mentioned description, and should be limited by the claim.